

Redox reactions with bis(η^6 -arene) derivatives of early transition metals

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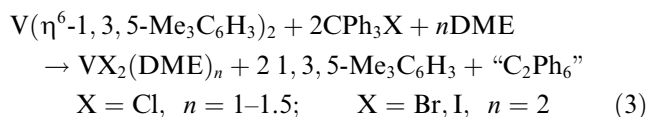
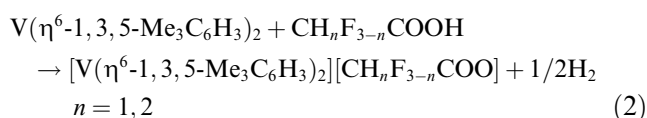
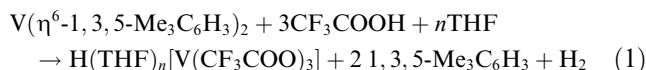
Abstract

The reactivity of $M(\eta^6\text{-arene})_2$ derivatives of early transition metals ($M = \text{Ti, Cr, Mo, arene} = \text{MeC}_6\text{H}_5$; $M = \text{V, Nb, arene} = 1,3,5\text{-Me}_3\text{C}_6\text{H}_3$) has been investigated and the syntheses of new and known compounds are described. The derivatives $M(\text{CH}_3\text{COO})_3$, $M = \text{Ti, V, Nb, Cr}$; $M(\text{CF}_3\text{COO})_3$, $M = \text{Ti, Nb, Cr}$; $M(\text{acac})_3$, $M = \text{Ti, V, Mo}$, acac = acetylacetonato, and $M(\text{F}_6\text{acac})_3$, $\text{F}_6\text{acac} = \text{hexafluoroacetylacetonato}$, $M = \text{V, Nb}$ have been prepared by reaction of the metal bis(arene) derivatives with the appropriate Lewis acid. The crystal and molecular structure of $\text{V}(\text{F}_6\text{acac})_3$ has been determined. Hydrogen halides or halogens react with $M(\eta^6\text{-arene})_2$ with formation of metal halides, a highly reactive form of VCl_3 being obtained from $\text{V}(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ and hydrogen chloride in heptane. TiCl_4 oxidizes $\text{Ti}(\eta^6\text{-arene})_2$ with complete loss of the arene ligands. An electron transfer process affording ionic derivatives of formula $[\text{M}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{TiCl}_4(\text{THF})_2]$, $M = \text{Cr}$ (structurally characterized), Mo , has been observed between the THF-adduct of TiCl_4 and the appropriate metal-arene derivative of Group 6.
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Keywords: Early transition elements; Arene; Oxidation; Reactivity; Structure

1. Introduction

Recent contributions from us and from these laboratories have described the use of transition metal complexes in low oxidation states as precursors to organometallic, inorganic or coordination compounds [1]. As far as bis(η^6 -arene) derivatives are concerned, we have shown that the treatment of $\text{V}(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ with CF_3COOH in THF or triphenylmethyl halides in DME [1k–1n] proceeds with loss of the arene ligands affording vanadium(I) and vanadium(II) derivatives according to the following equations:



Monoelectronic oxidizing agents such as $[\text{FeCp}_2]^+$ [2] or Ag^+ [3] react with $\text{Ti}(\eta^6\text{-}1,3,5\text{-}^i\text{Pr}_3\text{C}_6\text{H}_3)_2$ or $\text{V}(\eta^6\text{-arene})_2$ (arene = $1,3,5\text{-Me}_3\text{C}_6\text{H}_3$, $1,3,5\text{-}^t\text{Bu}_3\text{C}_6\text{H}_3$) giving the $[\text{M}(\eta^6\text{-arene})_2]^+$ cations. Similarly, bis(η^6 -arene) compounds of niobium(0) afford $[\text{Nb}(\eta^6\text{-arene})_2]^+$, $L = \text{CO}$, alkynes, PMe_3 [4].

As it is now possible to prepare gram quantities of $\text{M}(\eta^6\text{-arene})_2$ ($M = \text{V, Nb}$, arene = $1,3,5\text{-trimethylbenzene}$; $M = \text{Cr, Mo}$, arene = toluene) via the Fischer–Hafner synthesis, i.e., by using conventional laboratory

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techniques, see Section 4, we became interested in further developing the use of low-valent bis(arene) metal complexes as precursors to classical inorganic or coordination compounds. This study appeared of interest especially when considering that some of our recent results show that VCl_2 [1n], as obtained from $V(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ at room temperature or below, has a higher reactivity with respect to commercial compounds due to the stabilization of metastable crystalline phases. Being interested in looking for periodic trends in the behaviour of the arene derivatives, we have also examined the reactivity of $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$, as prepared via the metal vapour synthesis (MVS) technique [5].

In this paper, we report the reactions of bis(η^6 -arene) derivatives of Groups 4, 5 and 6 elements with substances containing active protons such as carboxylic acids or β -diketones and a variety of oxidizing species, namely halogens, triphenylmethyl halides, and transition metal-based reagents, e.g., $TiCl_4$.

2. Results and discussion

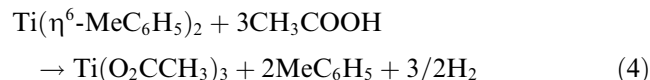
2.1. $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$

The available data concerning the reactivity of bis-arene derivatives of titanium(0) are limited. Reduction to the $[Ti(\eta^6\text{-arene})_2]^-$ anion (arene = C_6H_6 and MeC_6H_5) can be achieved by using a potassium film [6]. Oxidation to the $[Ti(\eta^6\text{-arene})_2]^+$ cation was reported only in the case of $Ti(\eta^6\text{-}1,3,5\text{-}^i\text{Pr}_3\text{C}_6\text{H}_3)_2$ by the reaction with ferricinium derivatives [2]. All other reactions involving the oxidation of the metal centre resulted in the loss of the aromatic ligand. For example, the reaction of $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ with CO_2 was reported to afford an oxalato derivative of low-valent titanium [7], whereas the reactions with acetylacetone and hydrogen sulfide or sulfur gave the corresponding complexes of titanium(III), $Ti(\text{acac})_3$ and Ti_2S_3 , respectively [8]. The bis-cyclopentadienyl derivative of titanium(III) $[TiCp_2Cl]_2$ was obtained by reacting $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ with $TiCp_2Cl_2$ [8], and both $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ and $Ti(\eta^6\text{-}1,3,5\text{-}^i\text{Bu}_3\text{C}_6\text{H}_3)_2$ gave TiI_4 with I_2 [9].

The reaction of the titanium(0) arene complexes with carboxylic acids was anticipated to produce carboxylato derivatives of titanium, whose chemistry is well established, although only $TiCp_2(O_2CCF_3)_2$, $TiO(O_2CCF_3)_2$ [10,11], the titanium(III) species $Ti(O_2CCH_3)_{3-n}Cl_n$ [12] and the corresponding trifluoro-substituted ones [11] have been thoroughly characterized. As far as the homoleptic trifluoroacetato derivatives $Ti(O_2CCF_3)_n$ are concerned, $Ti(O_2CCF_3)_4$ does not appear to have been prepared as yet, although the corresponding zirconium and hafnium derivatives are known [11], and both

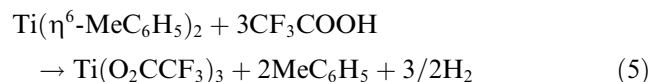
$Ti(O_2CCF_3)_3$ and $Ti(O_2CCF_3)_2$ have been mentioned but not characterized [11].

Addition of a slight excess of CH_3COOH to a solution of $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ in toluene resulted in the immediate precipitation of the light green $Ti(O_2CCH_3)_3$ (see Eq. (4)).



The solid-state IR spectrum shows three strong absorptions in the typical range ($1800\text{--}1300\text{ cm}^{-1}$) of the carboxylate stretching vibrations, at 1618, 1544 and 1455 cm^{-1} . Based on the data reported in the literature and on the separation (Δ) between the asymmetric and the symmetric stretching vibrations [13], the absorptions are assigned to the asymmetric stretching of a bridging acetato group, the asymmetric stretching of a chelating acetato group and to the symmetric stretching of both groups, respectively. The presence of bridging acetato groups suggests a polynuclear structure for this compound, even though its solubility in toluene excludes the possibility of a high nuclearity. The magnetic moment (0.99 BM at 296 K), much lower than the expected value (1.73 BM) for a compound containing a metal cation of d^1 configuration, can be explained on the basis of interactions between neighbouring titanium atoms through the π system of the carboxylato bridges.

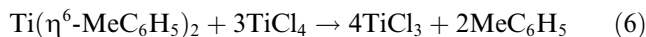
When a solution of $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ in toluene was treated with CF_3COOH , a green-brown solid precipitated out. Although the presence of trifluoroacetato groups was confirmed by IR, elemental analyses were not reproducible. In a coordinating solvents, such as THF, addition of CF_3COOH to a freshly prepared solution of $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ resulted in an immediate reaction with formation of a brick red solution, from which solid $Ti(O_2CCF_3)_3$ could be isolated (Eq. (5)).



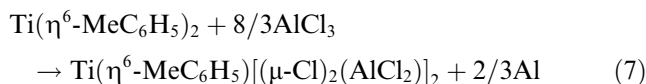
The IR spectrum of the solid shows two strong absorptions at 1698 and 1485 cm^{-1} , assigned to the asymmetric and symmetric C–O stretching vibrations, and two strong absorptions at 1208 and 1165 cm^{-1} , assigned to the C–F stretching vibrations of the trifluoromethyl group. The separation of the C–O stretching vibrations ($\Delta\nu \sim 215\text{ cm}^{-1}$) indicates the presence of either chelating or bridging trifluoroacetato groups. The polynuclear nature of the compound is also evidenced by the strongly reduced magnetic moment of the compound (0.86 BM at 292 K), as compared to the value of 1.73 BM expected for a Ti(III) centre of d^1 electronic configuration.

The tendency of titanium(0) in $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ to attain the +III oxidation state was further confirmed by the reaction of $Ti(\eta^6\text{-MeC}_6\text{H}_5)_2$ with $TiCl_4$, which

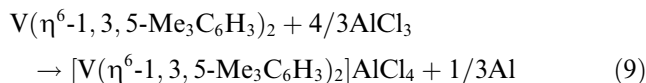
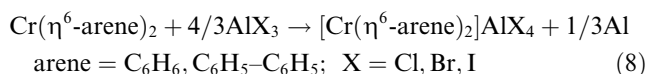
affords substantially amorphous [14] TiCl_3 as a brown solid (Eq. (6)).



$\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$ reacts with AlCl_3 as well, the reaction products being the well-established derivative of titanium(II) $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)[(\mu\text{-Cl})_2(\text{AlCl}_2)]_2$ [15] and aluminum (Eq. (7)).



This reactivity parallels the reactions of bis-arene derivatives of vanadium(0) [16] and chromium(0) [17] with aluminum trichloride, see Eqs. (8) and (9). The different reactivity of the chromium, vanadium and titanium systems

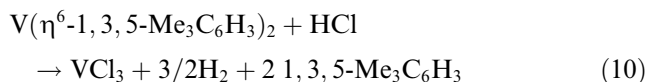


can be explained by considering that the primary products of the Fischer–Hafner reductions are the $[\text{M}(\eta^6\text{-arene})_2]^+$ cations in the case of vanadium and chromium [16], while the reaction of TiX_4 with Al/AlX_3 in arene gives the titanium(II) derivatives $\text{Ti}(\eta^6\text{-arene})[(\mu\text{-X})_2(\text{AlX}_2)]_2$, $\text{X} = \text{Cl, Br, I}$ [15,18].

2.2. $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$

The η^6 -arene derivatives of vanadium(0) were reported to react with alcohols such as ethylene glycol and glycerine, or with dithioacetic acid to afford vanadium(III) compounds of formula $\text{V}(\text{OR})_3$ [19] or $(\text{CH}_3\text{CS}_2)_2\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}(\text{S}_2\text{CCH}_3)_2$ [20], respectively. Oxidation to vanadium(II) occurs when $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ is reacted with CF_3COOH in heptane or THF [1m] or with triphenylmethyl halides in DME [11] (see Eqs. (1)–(3)).

The vanadium(0) complex $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ rapidly reacts with hydrogen chloride at room temperature in heptane affording quantitative yields of an almost amorphous form of VCl_3 [14] (Eq. (10)), which reacts vigorously with THF affording $\text{VCl}_3(\text{THF})_3$ [21] within the time of mixing the reagents at ca. -30°C .

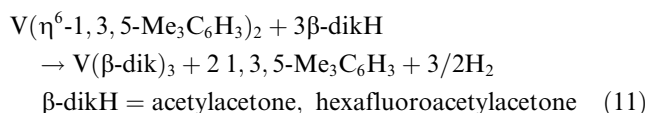


However, the heavier hydrogen halides HX ($\text{X} = \text{Br, I}$) in heptane afford mixtures of $[\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2]\text{X}$, VX_2 and VX_3 . On changing the medium with a coordinating one (DME), the reaction does not proceed beyond the oxidation to vanadium(II) and high yields of

$\text{cis-VX}_2(\text{DME})_2$, $\text{X} = \text{Br, I}$ [11], were obtained. It has to be noticed that intractable oily substances were obtained when a HX/V molar ratio higher than 2 was used.

The reaction of $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ with neat CH_3COOH [22] is fast and exothermic giving a green solid almost insoluble in the common organic solvents which has been identified as $\text{V}(\text{O}_2\text{CCH}_3)_3$. A compound of similar properties, formulated as $\text{V}_2(\text{O}_2\text{CCH}_3)_6$, was reported to be formed by the reaction of VB_2 with acetic acid at 110°C for 2 weeks [23]. The magnetic moment of our compound is 2.64 BM at 296 K, slightly reduced with respect to the spin-only value (2.84 BM) calculated for a vanadium(III) ion of d^2 configuration, probably due to spin coupling through bridging acetates.

β -Diketones react with $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ giving β -diketonato derivatives [24] of vanadium(III), see Eq. (11), the reaction rates being related to the acid strength of the diketone itself. Acetylacetone ($\text{p}K_a = 8.80$) [25] reacts at appreciable rate only as a neat liquid at the boiling point of the mixture, while hexafluoroacetylacetone ($\text{p}K_a = 4.35$) [25] quickly evolves dihydrogen when treated with an heptane solution of $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ at room temperature.



The molecular structure of $\text{V}(\text{F}_6\text{acac})_3$ has been solved by X-ray diffraction methods. It consists of discrete molecules separated by normal intermolecular contacts. Within each molecule (Fig. 1), the central metal atom is surrounded by the six oxygen atoms of the three β -diketonato ligands. The V–O bond distances (mean

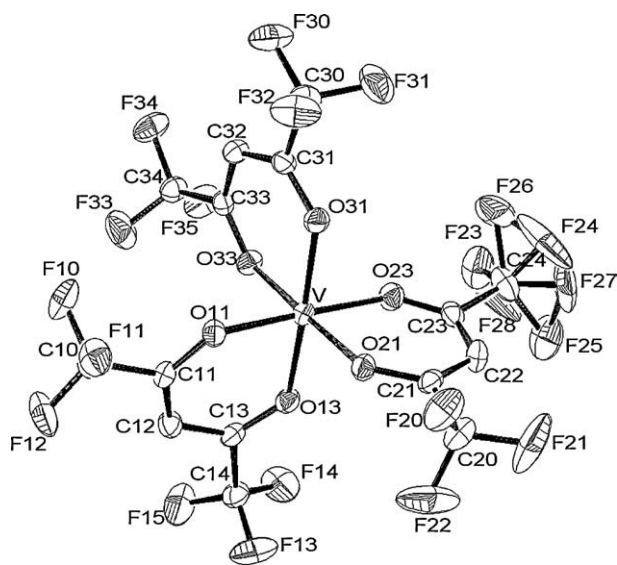


Fig. 1. ORTEP [26] view of tris(1,1,1,5,5,5-hexafluoroacetylacetonate)vanadium(III), $\text{V}(\text{F}_6\text{acac})_3$. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted.

Table 1

Bond distances (Å) and angles (°) in tris(1,1,1,5,5,5-hexafluoroacetylacetonate)vanadium(III), V(F₆acac)₃

V–O(11)	1.962(2)	O(33)–V–O(31)	87.92(9)
V–O(33)	1.963(2)	O(11)–V–O(23)	178.19(10)
V–O(31)	1.980(2)	O(33)–V–O(23)	92.77(10)
V–O(23)	1.987(2)	O(31)–V–O(23)	89.76(10)
V–O(13)	1.991(2)	O(11)–V–O(13)	87.90(9)
V–O(21)	1.995(2)	O(33)–V–O(13)	90.06(9)
O(11)–C(11)	1.265(4)	O(31)–V–O(13)	177.74(9)
O(13)–C(13)	1.250(4)	O(23)–V–O(13)	91.34(10)
O(21)–C(21)	1.255(4)	O(11)–V–O(21)	91.70(10)
O(23)–C(23)	1.246(4)	O(33)–V–O(21)	179.33(9)
O(31)–C(31)	1.259(4)	O(31)–V–O(21)	91.72(9)
O(33)–C(33)	1.266(4)	O(23)–V–O(21)	86.67(9)
		O(13)–V–O(21)	90.32(10)
		O(11)–V–O(33)	88.87(10)
		O(11)–V–O(31)	91.06(10)

Numbers in parenthesis refer to the least significant digits.

value: 1.979 Å) and the O–V–O angles (mean value 88.6°) indicate a *quasi*-regular octahedral coordination of the vanadium atom (see Table 1).

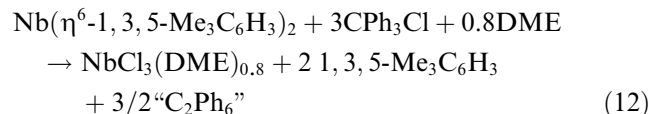
Structurally characterized vanadium(III) β-diketonato complexes are not common in the literature, examples being V(acac)₃ [27] and V(CF₃COCHC(O)CH₃)₃ [28]. Moreover, the V(β-diketonato)₃ unit has been found in the vanadium(IV) complexes [V(acac)₃]SbCl₆ and [V(Bzacac)₃]SbCl₆ (BzacacH = 1-phenylbutane-1,3-dione) [29]. The VO₆ units in V(acac)₃, [V(acac)₃]⁺ and [V(Bzacac)₃]⁺ show a tetragonal distortion (two of the six V–O bond distances are significantly shorter than the other) which is not present in V(F₆acac)₃, where the average values of the equatorial and axial V–O distances are identical within experimental error (1.979 and 1.975 Å, respectively). The bidentate ligands are substantially planar, with maximum deviation of 0.129 Å for O(11).

2.3. Nb(η⁶-1,3,5-Me₃C₆H₃)₂

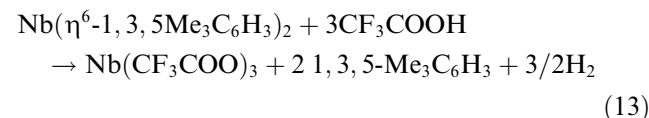
Bis-arene derivatives of niobium(0) have been studied in recent years, mainly concerning the monoelectronic Nb(0) → Nb(I) oxidation, a reaction which proceeds without loss of coordinated arene [4]. On the other hand, little is known about the exhaustive oxidation of niobium(0). To the best of our knowledge, only the reaction of Nb(η⁶-1,3,5-Me₃C₆H₃)₂ with di-iodine has been reported, giving the dinuclear neutral compound of Nb(II), Nb₂(η⁶-1,3,5-Me₃C₆H₃)₂(μ-I)₄ [30], or NbI₅ [9], depending on the I₂/Nb molar ratio.

The reaction of Nb(η⁶-1,3,5-Me₃C₆H₃)₂ with three equivalents of CPh₃Cl in DME forms NbCl₃(DME)_{0.8} [31], and “C₂Ph₆” [32,33], see Eq. (12). It is important to note that neither the reaction with CPh₃Cl in heptane or toluene nor the use of CPh₃Br afforded pure compounds. Mixture of halides were obtained also by react-

ing Nb(η⁶-1,3,5-Me₃C₆H₃)₂ with dry hydrogen halides in a hydrocarbon or in coordinating solvents. Moreover, attempts to perform a monoelectronic oxidation to the [Nb(η⁶-1,3,5-Me₃C₆H₃)₂]⁺ cation failed: niobium(0) was still present in the reaction mixture after prolonged reaction times.

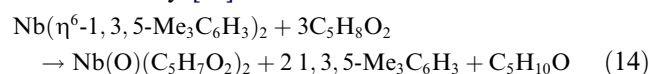


The same oxidation state of the metal (+III) is attained in the reaction of Nb(η⁶-1,3,5-Me₃C₆H₃)₂ with CF₃COOH, the product being identified as Nb(CF₃COO)₃ (see Eq. (13)).

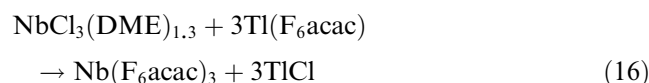
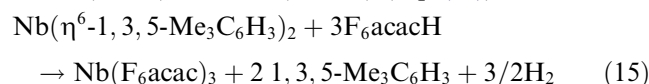


The relative positions of the symmetric and asymmetric C=O stretching modes (IR absorptions are observed at 1635 and 1460 cm⁻¹) suggest a bidentate coordination of the trifluoroacetato ligand, thus suggesting this derivative to be a hexacoordinated compound of niobium(III). No pure product was isolated from the reaction with acetic acid under the same experimental conditions (hydrocarbons or THF or DME).

The reaction of Nb(η⁶-1,3,5-Me₃C₆H₃)₂ with acetylacetone was conducted at the reflux temperature of the mixture: instead of the expected Nb(acac)₃, the oxo-acetylacetonato of niobium(IV) Nb(acac)₂(O) was obtained. The isolation of this compound suggests that deoxygenation of the organic ligand takes place. As a matter of fact, detectable amounts of 2-pentanone (C₅H₁₀O, GCMS) were present in the reaction mixture, thus suggesting the overall stoichiometry of Eq. (14). Furthermore, the analysis of the IR spectrum of the solid inorganic product allowed us to identify a broad band of medium intensity centred at 930 cm⁻¹, typical of complexes containing the Nb=O moiety [34].



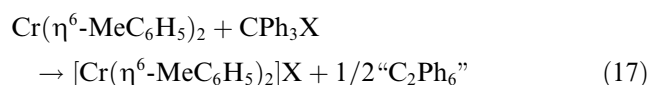
The reaction of Nb(η⁶-1,3,5-Me₃C₆H₃)₂ with F₆acacH proceeds smoothly at room temperature with dihydrogen evolution and formation of the niobium(III) derivative Nb(F₆acac)₃, see Eq. (15). This new compound has also been prepared, albeit in low yields, from NbCl₃(DME)_{1.3} and Tl(F₆acac) (Eq. (16)).



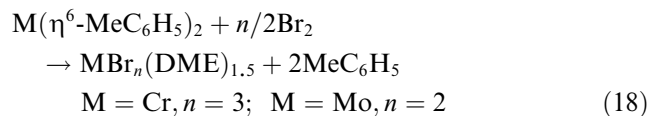
Nb(F₆acac)₃ is not as volatile as the corresponding vanadium compound, suggesting a higher nuclearity for the niobium derivative. Strictly connected is the observation that both compounds are paramagnetic, but the magnetic moment of the vanadium species (2.62 BM at 296 K) is close to the value expected for a 3d³ system (2.84 BM), while the corresponding niobium derivative shows a reduced magnetic moment of 0.89 BM (295 K) which is well reduced with respect to the expected value. These data strongly suggest that Nb(F₆acac)₃ has a polynuclear structure, probably containing bridging hexafluoroacetylacetonato ligands as observed in some silver(I) compounds such as [Ag(1,5-COD)(F₆acac)]₂, 1,5-COD = 1,5-cyclooctadiene [35], [Ag(Me₂COD)(F₆acac)]₂, Me₂COD = 1,5-dimethylcycloocta-1,5-diene [36], [Ag₂(μ₂-F₆acac)₂(diglyme)₂] [37], and Ag₂(μ₂-F₆acac)(μ₂-CF₃COO)(diglyme)₂] [37].

2.4. M(η⁶-MeC₆H₅)₂, M = Cr, Mo

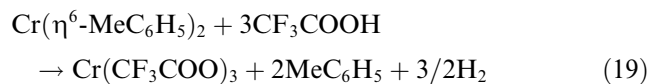
At variance to niobium and vanadium [11], the reaction between Cr(η⁶-MeC₆H₅)₂ and CPh₃X results in a mono-electronic oxidation of the chromium(0) derivative [32]. By adding one equivalent of CPh₃X to the solution of Cr(η⁶-MeC₆H₅)₂, the deep yellow [Cr(η⁶-MeC₆H₅)₂]X (X = Br, Cl) [38], Eq. (17), was identified.



Total loss of the arene rings was brought about by bromine: the reaction affords intractable mixtures when performed in hydrocarbons. However, in dimethoxyethane, products were obtained which were identified as the chromium(III) and the molybdenum(II) bromides, CrBr₃(DME)_{1.5} and MoBr₂(DME)_{1.5}, respectively (Eq. (18)).



With trifluoroacetic acid, Cr(η⁶-MeC₆H₅)₂ gave Cr(CF₃COO)₃ which was isolated and characterized, see Eq. (19).

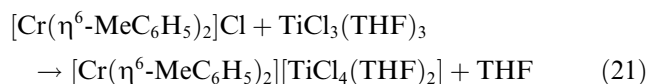
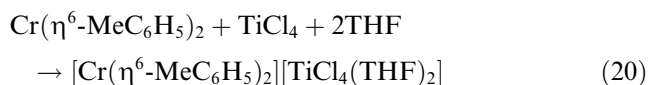


Molybdenum acetylacetonate Mo(acac)₃ [39] resulted from the reaction of Mo(η⁶-MeC₆H₅)₂ with acacH.

Some years ago, it was reported that metal carbonyls such as V(CO)₆, Cr(CO)₆ and Mo(CO)₆ react with TiCl₄ to give binary chlorides of general formula MCl_n·n-TiCl₃ [40]. Some of us, have extended this reaction to V(η⁶-1,3,5-Me₃C₆H₃)₂ showing the formation of solid compounds of general formula VTi_nCl_m, with n and m

depending on the V(η⁶-1,3,5-Me₃C₆H₃)₂/TiCl₄ molar ratio [41]. Mixed niobium/titanium halides of general formula NbTi_nCl_m were obtained with Nb(η⁶-1,3,5-Me₃C₆H₃)₂, the composition depending on the Nb/Ti molar ratio [42]. As far as arene derivatives of Group 6 are concerned, the interaction between Cr(η⁶-C₆H₆)₂ and TiCl₄ gives a product able to promote the polymerization of iso-butylvinyl ether [43], the real nature of the Cr/Ti species not being established. It appeared therefore of interest to examine the reactivity of Group 6 metal arenes with TiCl₄.

When a heptane solution of TiCl₄ was added to an equimolar amount of Cr(η⁶-MeC₆H₅)₂ in the same solvent a quick reaction took place with formation of a bulky grey solid: neither chloride ions nor toluene were found in solution, thus suggesting that both chromium and titanium had been incorporated in the precipitate. The grey solid is almost insoluble in hydrocarbons and it is extremely moisture sensitive, turning yellow and partially dissolving in THF. Work up of the reaction mixture afforded [Cr(η⁶-MeC₆H₅)₂][TiCl₄(THF)₂], see Eq. (20), whose IR spectrum shows arene CH stretching at 3059 and 2982 cm⁻¹ and two strong bands (1020–860 cm⁻¹) due to coordinated THF. The compound was prepared also by reacting [Cr(η⁶-MeC₆H₅)₂]Cl with TiCl₃(THF)₃ (see Eq. (21)).



The product was characterized by X-ray single-crystal diffraction and its structure is shown in Fig. 2; a selection of bond distances and angles is in Table 2.

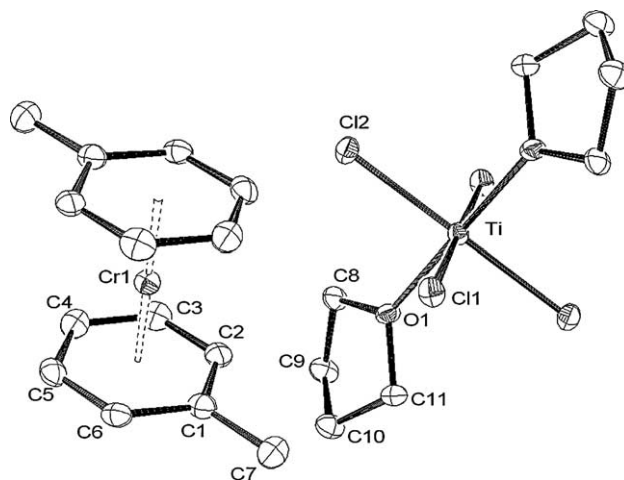


Fig. 2. ORTEP [26] view of [Cr(η⁶-MeC₆H₅)₂][TiCl₄(THF)₂]. Displacement ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted.

Table 2
Bond distances (Å) and angles (°) in $[\text{Cr}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{TiCl}_4(\text{THF})_2]$

Ti–O(1)	2.082(2)	O(1)#1–Ti–Cl(2)#1	88.75(7)
Ti–Cl(2)	2.4018(9)	O(1)–Ti–Cl(2)#1	91.25(7)
Ti–Cl(1)	2.4083(10)	O(1)#1–Ti–Cl(1)	89.11(7)
O(1)–C(11)	1.457(4)	O(1)–Ti–Cl(1)	90.89(7)
O(1)–C(8)	1.473(4)	Cl(2)#1–Ti–Cl(1)	90.34(3)
Cr(1)–C(3)	2.124(4)	Cl(2)–Ti–Cl(1)	89.66(3)
Cr(1)–C(2)	2.132(3)	C(11)–O(1)–C(8)	109.3(2)
Cr(1)–C(4)	2.139(3)	C(11)–O(1)–Ti	123.36(19)
Cr(1)–C(5)	2.144(3)	C(8)–O(1)–Ti	127.05(19)
Cr(1)–C(6)	2.153(3)	O(1)–C(8)–C(9)	104.6(3)
Cr(1)–C(1)	2.169(3)		

Numbers in parenthesis refer to the least significant digits. Symmetry transformations used to generate equivalent atoms: #1: $-x, -y + 1, -z + 1$; #2: $-x + 1, -y + 1, -z$.

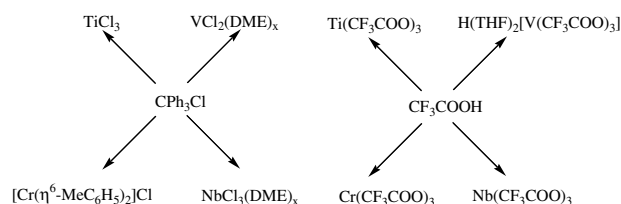
The structure consists of discrete $[\text{Cr}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cations and $[\text{TiCl}_4(\text{THF})_2]^-$ anions. The chromium atom is sandwiched between two staggered toluene rings which represents the conformation generally adopted by alkyl-substituted arene complexes of Cr(I) [44]. The Cr–centroid distance (1.615 Å) and the Cr–C distances (2.144 Å, mean value) are similar to those observed in other chromium(I) bis(toluene) derivatives [44].

As far as the $[\text{TiCl}_4(\text{THF})_2]^-$ anion is concerned, the average Ti–Cl (2.405 Å) and Ti–O (2.083 Å) bond distances are comparable to those reported for the same anion in the $[\text{Bu}_4\text{N}]^+$ derivative (2.394 and 2.099 Å, respectively) [45]. Some relevant differences are noted on comparing the Ti(III) derivative with the parent neutral molecule of titanium(IV) *trans*- $\text{TiCl}_4(\text{THF})_2$, whose Ti–Cl distances are notably shorter (2.293 Å) [46].

The reaction of $\text{Mo}(\eta^6\text{-MeC}_6\text{H}_5)_2$ with TiCl_4 proceeds similarly, i.e., with immediate precipitation of a bulky grey solid, which turned green on changing the solvent from heptane to THF. The compound was identified as $[\text{Mo}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{TiCl}_4(\text{THF})_2]$ on the basis of elemental analysis and on the similarity of its IR spectrum with that of the chromium analogue. Several attempts to crystallize this product always produced twinned crystals.

3. Conclusions

The use of metal bis(arene) complexes as precursors to classical coordination compounds has been further developed. The recent publication of conventional, high-yielding syntheses of vanadium(0) and niobium(0) bis(η^6 -mesitylene) derivatives, together with the long-standing preparative method of the bis(η^6 -toluene) species of chromium and molybdenum, has allowed this chemistry to be explored in some detail. Moreover, some



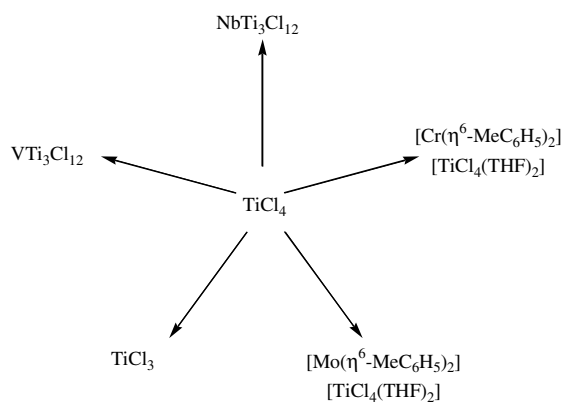
Scheme 1. Reactivity of metal bis(arene) complexes with CPh_3Cl and CF_3COOH .

reactions are reported of bis(η^6 -toluene)titanium(0), whose preparation still requires the use of MVS techniques.

Generally speaking, metal arenes can be converted to metal halides (or to their adducts with Lewis bases such as DME) by hydrogen halides, halogens and triphenylmethyl halides or to carboxylato or β -diketonato derivatives by carboxylic acids or substituted β -diketones, respectively. It has been found, for instance, that $\text{Nb}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ can be used as a starting material for the synthesis of $\text{NbCl}_3(\text{DME})_x$, as an alternative to the literature method [31]. Moreover, different acetato- and trifluoroacetato complexes can be obtained via redox reactions, which are high-yielding reactions and produce arenes and hydrogen only as by-products, thus favouring the recovery of the metal-containing product.

Zerovalent metal arene derivatives of early transition elements (Ti, V, Nb) easily lose coordinated arene ligands, a behaviour linked to their high tendency to undergo further oxidation (see Scheme 1).

In the reaction of $\text{M}(\eta^6\text{-arene})_2$ with TiCl_4 , $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$, $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ and $\text{Nb}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ undergo oxidation with loss of the arene ligands and formation of metal halides. The arene derivatives of Group 6, $\text{M}(\eta^6\text{-MeC}_6\text{H}_5)_2$, give the bis(η^6 -toluene) cations (see Scheme 2).



Scheme 2. Summary of the reactivity of TiCl_4 towards metal bis(η^6 -arene) complexes.

4. Experimental

4.1. General procedures

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. IR spectra were measured with the FT1725X instrument on or Nujol and/or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air. Magnetic susceptibility measurements were performed with a Faraday balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as standard. Pascal contributions were used to calculate the diamagnetic correction [47].

Hydrogen halides (Matheson), bromine (Carlo Erba, Milan), CH_3COOH (Carlo Erba, Milan), CF_3COOH (Carlo Erba, Milan), CPh_3Cl (Aldrich) and CPh_3Br (Aldrich) were used as received. TiCl_4 (Aldrich) was distilled prior to use. AlCl_3 was sublimed prior to use and stored in ampoules sealed under a dinitrogen atmosphere. Acetylacetone, acacH , and hexafluoroacetylacetone, F_6acacH , were distilled prior to use. The following compounds were prepared as reported in the literature: $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$ [5], $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ [16], $\text{Nb}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ [48], $\text{M}(\eta^6\text{-MeC}_6\text{H}_5)_2$, $\text{M} = \text{Cr}$ [16], Mo [16], $\text{TiCl}_3(\text{THF})_3$ [49], $\text{TiCl}_4(\text{THF})_2$ [49], $\text{NbCl}_3(\text{DME})_{1.3}$ [31]. The experimental procedure [50] for preparing $\text{Ti}(\text{F}_6\text{acac})$ was modified as follows. A solution of TlOEt (2.8 mL, 9.9 g, 39.5 mmol) in toluene (50 mL) was added within 30 min to a solution of F_6acacH (5.7 mL, 8.4 g, 40.3 mmol) in toluene (40 mL). The yellow solution was evaporated to dryness and heptane (30 mL) was added to the residue. The solid was recovered by filtration and dried in vacuo affording 6.9 g (60% yield) of $\text{Ti}(\text{F}_6\text{acac})$.

4.2. Reactivity of $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$

4.2.1. CH_3COOH

A solution of $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.20 g, 0.86 mmol) in toluene (20 mL) was added of CH_3COOH (2 mL, 34.69 mmol). An immediate reaction took place with formation of a light green solid. After 2 h stirring at room temperature the solid was filtered off, washed with light petroleum and dried in vacuo. It was analytically and spectroscopically identified as $\text{Ti}(\text{CH}_3\text{COO})_3$ (0.10 g, 53% yield). Anal. Calc. for $\text{C}_6\text{H}_9\text{O}_6\text{Ti}$: C, 32.0; H, 4.0; Ti, 21.3. Found: C, 32.5; H, 3.8; Ti, 21.0%. IR (PCTFE and Nujol mull) $\tilde{\nu}/\text{cm}^{-1}$: 2930 m, 2861 w, 1618 s, 1544 vs, 1455 vs, 1347 ms, 1028 m, 803 w, 723w, 656 ms. $\chi_{\text{corr}}^{\text{M}} = 410 \times 10^{-6}$ cgsu; diamagnetic correction = -92×10^{-6} cgsu; μ_{eff} (296 K) = 0.99 BM.

4.2.2. CF_3COOH

A freshly prepared solution of $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.14 g, 0.60 mmol) in THF (20 mL) was added of CF_3COOH (0.43 mL, 5.50 mmol). An immediate reaction took place with formation of a red-brown solution. After 18 h stirring at room temperature, the solvent was evaporated in vacuo affording a brown oil. Addition of heptane (25 mL) caused the formation of a brick red solid, which was filtered off and dried in vacuo. It was analytically and spectroscopically identified as $\text{Ti}(\text{CF}_3\text{COO})_3$ (0.10 g, 42% yield). Anal. Calc. for $\text{C}_6\text{F}_9\text{O}_6\text{Ti}$: C, 18.6; H, 0.0; Ti, 12.4. Found: C, 19.4; H, 0.1; Ti, 11.7%. IR (PCTFE and Nujol mull) $\tilde{\nu}/\text{cm}^{-1}$: 1793 w, 1699 s, 1485 m, 1434 w, 1208 vs, 1165 vs, 862 m, 788 m, 728 s, 528 w, 508 w. $\chi_{\text{corr}}^{\text{M}} = 314 \times 10^{-6}$ cgsu; diamagnetic correction = -122×10^{-6} cgsu; $\mu_{\text{eff}} = 0.86$ BM (292 K). When the reaction was performed in toluene or heptane, green-brown solids were isolated with composition $\text{Ti}(\text{CF}_3\text{COO})_n$, $n = 2.5\text{--}2.8$ depending on drying conditions.

4.2.3. TiCl_4

A 0.1 M solution of TiCl_4 in heptane (26 mL, 2.60 mmol) was added to a solution of $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.20 g, 0.86 mmol) in heptane (20 mL). An immediate reaction took place with formation of a brown solid. After 18 h stirring at room temperature, the solid was recovered by filtration, washed with heptane (10 mL) and dried in vacuo. It was analytically identified as TiCl_3 (0.39 g, 62% yield). Anal. Calc. for Cl_3Ti : Cl, 68.9; Ti, 31.1. Found: Cl, 69.2; Ti, 30.4%.

4.2.4. AlCl_3

AlCl_3 (2.1 g, 15.7 mmol) was added to a solution of $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)_2$ (1.4 g, 6.2 mmol) in toluene (100 mL). A slow reaction took place with formation of a black sticky solid, while colour fading of the solution was noticed. After 18 h stirring at room temperature, the solid was separated by filtration from the dark purple solution, washed with toluene (5×5 mL), dried in vacuo and identified as aluminum metal (0.095 g, 85% yield). The solution was evaporated to dryness, the purple solid washed with heptane (25 mL) and dried in vacuo. It was identified (Cl and Ti) as $\text{Ti}(\eta^6\text{-MeC}_6\text{H}_5)-[(\mu\text{-Cl})_2(\text{AlCl}_2)]_2$ (2.36 g, 80% yield) [15b].

4.3. Reactivity of $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$

4.3.1. Hydrogen chloride in heptane

A red brown solution of $\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ (2.2 g, 7.6 mmol) in heptane (100 mL) was treated with dry hydrogen chloride, with immediate decolouration of the solution and formation of the dark violet VCl_3 . After 2 h, the suspension was filtered and the solid was dried in vacuo at room temperature affording 1.17

g (98%) of VCl_3 . Anal. Calc. for Cl_3V : Cl, 67.6; Ti, 32.4. Found: Cl, 67.7; V, 32.3%.

4.3.2. Hydrogen halides (HBr, HI) in 1,2-dimethoxyethane

A solution of $V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.507 g, 1.74 mmol) in DME (25 mL) was treated with 3.43 mmol of dry hydrogen bromide introduced in the reaction flask through a silicon cap. An immediate reaction with formation of a green solid in a pale green solution was obtained. The solid was filtered and dried in vacuo at room temperature affording 0.523 g (77% yield) of *cis*- $VBr_2(dme)_2$ [11] (IR and elemental analysis) as a green microcrystalline solid.

cis- $VI_2(dme)_2$ [11] was obtained as a green solid (80% yield, IR and elemental analysis) by a similar procedure.

4.3.3. CH_3COOH

$V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (2.23 g, 7.6 mmol) was added to glacial acetic acid (44.7 g, 7.4 mol). An exothermic reaction took place with formation of a pale green solid. After 30 min stirring at room temperature, the suspension was filtered and the solid was washed with heptane (3×5 mL) and dried in vacuo at room temperature affording 1.616 g (93% yield) of $V(O_2CCH_3)_3$ in the form of a pale green, moisture-sensitive solid almost insoluble both in polar and non-polar organic solvents. Anal. Calc. for $C_6H_9O_6V$: C, 31.6; H, 4.0; V, 22.3. Found: C, 31.0; H, 4.0; V, 23.1%. IR (PCTFE and Nujol mull) $\tilde{\nu}/cm^{-1}$: 2988 w, 2934 w, 1753 ms, 1548 vs, 1452 vs, 1422 s, 1170 s, 1029 s, 869 s, 663 vs, 428 s, 493 ms. $\chi_{corr}^M = 2928 \times 10^{-6}$ cgsu; diamagnetic correction = -101×10^{-6} cgsu; μ_{eff} (296 K) = 2.64 BM.

4.3.4. *acacH*

$V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (1.95 g, 6.7 mmol) was dissolved in neat acetylacetone (29.25 g, 0.29 mmol). No reaction was observed after 2 h stirring at room temperature. After refluxing for 5 h, a brown solution was obtained. The excess acetylacetone was removed in vacuo at room temperature and the residue was suspended in heptane (25 mL). The resulting suspension was filtered and the solid was dried in vacuo at room temperature and identified as $V(acac)_3$ [24a,24c] (1.67 g, 73% yield) from analytical (C, H, and V analysis) and spectroscopic data (IR spectroscopy). $\chi_{corr}^M = 3534 \times 10^{-6}$ cgsu; diamagnetic correction = -101×10^{-6} cgsu; μ_{eff} (296 K) = 2.90 BM.

4.3.5. F_6acacH

$V(\eta^6-1,3,5-Me_3C_6H_3)_2$ (0.369 g, 1.27 mmol) was dissolved in heptane (25 mL) and treated with F_6acacH (0.79 g, 3.80 mmol) at room temperature. An immediate reaction took place with formation of a dark solid in a pale green solution. The suspension was filtered and

the solid was dried in vacuo at room temperature and identified as $V(F_6acac)_3$ [24b–24d] (0.381 g, 45% yield) from elemental analysis (C, H) and spectroscopic data (IR spectroscopy). $\chi_{corr}^M = 2878 \times 10^{-6}$ cgsu; diamagnetic correction = -241×10^{-6} cgsu; μ_{eff} (296 K) = 2.62 BM.

4.3.6. Crystal structure of $V(F_6acac)_3$: solution and refinement

Deep red crystals of $V(F_6acac)_3$ were grown by slow sublimation at $25^\circ C/10^{-2}$ mmHg. Diffraction data were collected at $-70^\circ C$ with an automatic diffractometer ENRAF-NONIUS CAD4 by the ω -scan method in the range $3.0 \leq \theta \leq 28^\circ$ using graphite-monochromatized Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Crystal data are reported in Table 3. The structure model was obtained by conventional heavy atom methods [51], completed by Fourier difference syntheses, and refined with full-matrix least-squares on F^2 [52]. Hydrogen atoms were calculated in idealized positions and allowed to ride on their carbon atoms with freely refined isotropic displacement parameters. Convergence was reached for 5282 reflections and 391 variables at $wR_2 = 0.1398$ (all data), $R_1 = 0.0540$ [observations with $I > 2\sigma(I)$]. Maxima and minima from a final Fourier map were 0.394 and -0.449 e Å^{-3} .

Table 3

Crystal data and parameters of the structure solution of $V(F_6acac)_3$ and $[Cr(\eta^6-MeC_6H_5)_2][TiCl_4(THF)_2]$

Empirical formula	$C_{15}H_3F_{18}O_6V$	$C_{22}H_{32}Cl_4CrO_2Ti$
Formula weight	672.11	570.18
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	8.824(2)	8.072(2)
<i>b</i> (Å)	13.167(3)	8.182(2)
<i>c</i> (Å)	19.245(5)	10.192(3)
α (°)	90	69.916(5)
β (°)	91.90(2)	79.924(5)
γ (°)	90	88.993(5)
<i>V</i> (Å ³)	2234.8(9)	621.8(3)
<i>Z</i>	4	1
<i>D</i> _{calc} (Mg m ⁻³)	1.998	1.523
μ (mm ⁻¹)	0.626	1.205
Index ranges	$0 \leq h \leq 11$, $0 \leq k \leq 16$, $-25 \leq l \leq 25$	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$
Reflections collected	5601	7850
Independent reflections (<i>R</i> _{int})	5282 (0.020)	2717 (0.059)
Absorption correction	None	Empirical
Data/restraints/parameters	5282/0/391	2717/0/140
Goodness-of-fit on <i>F</i> ²	1.003	1.035
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0540$, $wR_2 = 0.1262$	$R_1 = 0.0422$, $wR_2 = 0.0865$
<i>R</i> indices (all data)	$R_1 = 0.1231$, $wR_2 = 0.1398$	$R_1 = 0.0644$, $wR_2 = 0.1057$

4.4. Reactivity of $Nb(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$

4.4.1. CPh_3Cl

After dissolving $Nb(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ (0.573 g, 1.7 mmol) in DME (25 mL), a solution of CPh_3Cl (1.470 g, 5.2 mmol) in DME (25 mL) was added dropwise. The colour of the solution changed from red to orange-yellow to brown followed by the formation of a brown precipitate. The brick-red solid was filtered, washed with heptane (2×5 mL), dried in vacuo and identified as $NbCl_3(DME)_{0.8}$. Anal. Calc. for $C_{3.2}H_8Cl_3NbO_{1.6}$: Cl, 39.2; Nb, 34.2. Found: Cl, 38.7; Nb, 34.8%.

4.4.2. CF_3COOH

A solution of CF_3COOH (7 mL, 1.2 mM in heptane) was diluted with toluene (50 mL), $Nb(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ (0.678 g, 2.0 mmol) was added. Immediate reaction was observed with colour change from red to brown-green. After stirring overnight, an abundant mustard solid was filtered, washed with toluene (2×5 mL) and dried in vacuo to afford the air-sensitive light brown $Nb(O_2CCF_3)_3$ (0.637 g, 72.6% yield). Anal. Calc. for $C_6F_9NbO_6$: C, 16.7; H, 0.0; Nb, 21.5. Found: C, 16.2; H, 0.1; Nb, 20.5%. IR (PCTFE and Nujol mull) $\tilde{\nu}/\text{cm}^{-1}$: 1646 s, 1635 ms, 1460 mw, 1205 s, 967 m, 857 w, 726 m.

4.4.3. $acacH$

$Nb(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ (0.584, 1.72 mmol) was dissolved in toluene (50 mL) and the resulting blood-red solution was added of $acacH$ (0.54 mL, 5.3 mmol) and the reaction mixture was stirred overnight. After this time, the resulting golden solution was concentrated under reduced pressure until an oily consistency was reached and heptane (50 mL) was added: a grey solid precipitated out, which was filtered, washed with heptane (2×5 mL) and dried in vacuo. After workup, grey $Nb(O)(acac)_2$ (0.370 g, 70% yield) was isolated and characterized by IR and elemental analysis. Anal. Calc. for $C_{10}H_{14}NbO_5$: C, 39.1; H, 4.6; Nb, 30.3. Found: C, 39.5; H, 5.4; Nb, 29.0%. IR (Nujol) $\tilde{\nu}/\text{cm}^{-1}$: 1689 m, 1592 s, 1530 s, 1278 m, 1146 m, 1018 w, 930 br,s, 837 s, 661 m. The liquid collected in a cold trap during the evaporation of the original solution was shown (GC-MS) to contain pentan-2-one.

4.4.4. F_6acacH

F_6acacH (0.7 mL, 4.9 mmol) was added to a blood-red solution of $Nb(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$ (0.544 g, 1.63 mmol) in heptane (50 mL). As soon as the β -diketone was added, a blue-green solid precipitated out. After 2 h stirring the suspension was filtered. The resulting blue-green $Nb(F_6acac)_3$ was dried in vacuo (0.787 g, 67% yield), Anal. Calc. for $C_{15}H_3F_{18}NbO_6$: C, 25.2; H, 0.4; Nb, 13.0. Found: C, 24.7; H, 1.2; Nb, 14.0%. IR (PCTFE and Nujol) $\tilde{\nu}/\text{cm}^{-1}$: 3152 mw,

1607 s, 1567 m, 1542 m, 1362 m, 1201 br, 1043 w, 969 s, 901 m, 740 w, 661 w. $\chi_{\text{corr}}^M = 331 \times 10^{-6}$ cgsu; diamagnetic correction = -246×10^{-6} cgsu; μ_{eff} (295 K) = 0.89 BM.

4.4.5. Preparation of $Nb(F_6acac)_3$ from $NbCl_3(DME)_{1.3}$ and $Tl(F_6acac)$

A suspension of $NbCl_3(DME)_{1.3}$ (0.415 g, 1.31 mmol) in heptane (100 mL) was added of $Tl(F_6acac)$ (1.61 g, 3.83 mmol). A pale yellow solid in a blue-green solution was obtained after 48 h stirring at room temperature. The solid was eliminated by filtration, and the solution was dried in vacuo affording $Nb(F_6acac)_3$ (0.17 g, 18% yield) whose IR spectrum was superimposable to that of the compound obtained as described in Section 4.4.4.

4.5. Reactivity of $Cr(\eta^6\text{-MeC}_6\text{H}_5)_2$

4.5.1. $TiCl_4$

To a brown-yellow solution of $Cr(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.710 g, 3 mmol) in heptane, $TiCl_4$ (0.35 mL, 3 mmol) was slowly added. Immediately, the solution turned to a bulky grey-green suspension; which was filtered. The solid was washed with heptane (2×10 mL) and dried in vacuo. After contacting with THF (60 mL), the solid turned its colour to bright yellow in a blue-green solution. The solid was filtered, washed with THF (2×5 mL) and dried in vacuo, obtaining 1.11 g (65% yield) of $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2][TiCl_4(THF)_2]$. Anal. Calc. for $C_{22}H_{32}Cl_4CrO_2Ti$: C, 46.3; H, 5.7; Cl, 24.9. Found: C, 46.0; H, 5.3; Cl, 25.1%. IR (Nujol) $\tilde{\nu}/\text{cm}^{-1}$: 3059 m, 2982 w, 1495 w, 1441 m, 1383 w, 1339 w, 1055 w, 1039 m, 1018 vs, 993 w, 860 vs, 818 vs, 683 m. $\chi_{\text{corr}}^M = 2.44 \times 10^{-3}$ cgsu, diamagnetic correction = -344×10^{-6} cgsu, μ_{eff} (299 K) = 2.45 BM.

The compound $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2][TiCl_4(THF)_2]$ was also obtained by the following method. The chloride $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2]Cl$ (0.148 g, 0.54 mmol) was suspended in THF (25 mL) and $TiCl_3(THF)_3$ (0.211 g, 0.57 mmol) was added. An immediate reaction was observed and the orange suspension quickly changed to a blue-green one: after 30 min stirring, the reaction mixture was filtered, obtaining a yellow solid that, after washing with heptane and drying in vacuo, was identified as $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2][TiCl_4(THF)_2]$ (0.226 g, 72.6% yield) by comparison of its IR spectrum with that of the compound reported above.

4.5.2. Crystal structure of $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2][TiCl_4(THF)_2]$: solution and refinement

Yellow tablets were obtained by slow cooling (243 K) of a THF/acetonitrile (1:1) solution. Data were collected at 110 K with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å, graphite monochromator) on a Bruker D8 goniometer with a SMART APEX CCD area detector on a crystal of

approximate dimensions $0.18 \times 0.18 \times 0.03$ mm. Crystal data are reported in Table 3. 7850 reflections were collected with the ω -scan method in the range $2.16^\circ \leq \theta \leq 26.99^\circ$. An empirical absorption correction (minimum transmission 0.8124, maximum transmission 0.9648) was applied with SADABS [53]. After merging, 2717 independent reflections remained for structure solution by direct methods [51]. The structure model was completed by Fourier difference syntheses and refined by full-matrix least-squares on F^2 [52]. Convergence was reached for 2717 reflections and 140 variables at agreement factors of $wR_2 = 0.1057$ (all data), $R_1 = 0.0422$ [observations with $I > 2\sigma(I)$]. Maximum and minimum from a final Fourier map were 0.464 and -0.396 eA^{-3} .

4.5.3. CPh_3X , $X = Br, Cl$

Only the reaction with CPh_3Cl is described in detail, that with CPh_3Br being conducted in a similar manner. A solution of CPh_3Cl (0.751 g, 2.7 mmol) in 10 mL of toluene was added into a toluene (25 mL) solution of $Cr(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.635 g, 2.7 mmol). The yellow-orange suspension immediately formed on addition of the reagent was filtered and the orange product $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2]Cl$ was washed with toluene (2×10 mL) and dried in vacuo. (0.507 g, 69% yield) and identified by analytical and spectroscopic data.

4.5.4. CF_3COOH

The compound $Cr(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.80 g, 3.4 mmol) was dissolved in DME (100 mL) and an excess of trifluoroacetic acid (1.3 mL, 17 mmol, in 25 mL DME) was added to the resulting brown-yellow solution. The mixture was refluxed for 12 h affording a dark green solution. After concentration, an oily substance was obtained which was added of heptane (50 mL). The mixture was stirred for 5 days at room temperature obtaining a green microcrystalline solid which gave correct analytical data for $Cr(CF_3COO)_3$, with an IR spectrum consistent with that of an authentic sample [54].

4.5.5. Bromine

The compound $Cr(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.702 g, 3 mmol) was dissolved in DME (125 mL) and a solution of Br_2 (0.24 mL, 4.5 mmol) in heptane (5 mL) was slowly added. The reaction mixture turned immediately yellow with formation of an abundant precipitate and then violet after 2 h stirring. The suspension was filtered and the solid washed with DME (2×5 mL). After drying in vacuo, $CrBr_3(DME)_{1.5}$ (1.164 g, 90% yield) was recovered as a violet microcrystalline solid. Anal. Calc. for $C_6H_{15}Br_3CrO_3$: Cr, 12.2; Br, 56.1. Found: Cr, 12.3; Br, 56.0%. IR (Nujol) $\tilde{\nu}/\text{cm}^{-1}$: 1067 s, 1025 s, 981 s, 854 s, 838 s.

4.6. Reactivity of $Mo(\eta^6\text{-MeC}_6\text{H}_5)_2$

4.6.1. $TiCl_4$

To a well-stirred solution of $Mo(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.463 g, 1.6 mmol) in heptane (50 mL), $TiCl_4$ (0.2 mL, 1.6 mmol, in 5 mL heptane) was added dropwise. Immediately, the solution became cloudy and changed to a bulky suspension within 5 min. The solid was filtered, washed with heptane, dried in vacuo and then treated with THF (50 mL). The resulting suspension was stirred overnight and the solid was recovered by filtration. After drying in vacuo, $[Mo(\eta^6\text{-MeC}_6\text{H}_5)_2][TiCl_4(THF)_2]$ (0.206 g, 20.6% yield) was isolated as a green microcrystalline solid. Anal. Calc. for $C_{22}H_{32}Cl_4MoO_2Ti$: C, 43.0; Br, 5.2; Cl, 23.1. Found: C, 43.5; H, 4.7; Cl, 22.6%. IR (Nujol) $\tilde{\nu}/\text{cm}^{-1}$: 3060 w, 1020 m, 862 m, 721 m, 669 m.

4.6.2. Bromine

To a solution of $Mo(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.409 g, 1.5 mmol) in DME (125 mL), bromine (0.11 mL, 4.5 mmol) in heptane (10 mL) was added dropwise. The resulting cloudy solution changed from green to yellow to brick-red in 2 h. The red-brown precipitate was recovered by filtration, washed with heptane (2×5 mL) and dried in vacuo (0.356 g, 60% yield). Anal. Calc. for $MoBr_2(DME)_{1.5}$, $C_6H_{15}Br_2MoO_3$: Mo, 24.5; Br, 40.9. Found: Mo, 24.1; Br, 39.6%. IR (Nujol) $\tilde{\nu}/\text{cm}^{-1}$: 1068 s, 1020 s, 970 m, 862 ms, 840 s.

4.6.3. *acacH*

$Mo(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.762 g, 2.7 mmol) was dissolved in neat *acacH* (2 mL). The green colour of the starting molybdenum complex quickly disappeared and a deep brown-red solution was obtained. After 1 h stirring at room temperature, excess pentan-2,4-dione was removed in vacuo and heptane (15 mL) was added. The mixture was cooled down to 243 K and filtered. The product $Mo(acac)_3$ (0.420 g, 38.9% yield) was recovered and identified analytically and by comparison of its IR spectrum with that reported in the literature [39].

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 263627 for $V(F_6acac)_3$ and CCDC 263628 for $[Cr(\eta^6\text{-MeC}_6\text{H}_5)_2][TiCl_4(THF)_2]$. Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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